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STUDIES OF GALLIUM NITRIDE, A LARGE BAND-GAP SEMICONDUCTOR

This thesis contains studies of growth techniques and of the crystallographic, thermal, optical and electrical properties of the III-V semiconductor GaN. The results obtained have been presented in the following papers:

- I. E. Ejder, Thermal Expansion of GaN, phys. stat. sol. (a) 23, (1974) (to be published).
- II. E. Ejder, Growth and Morphology of GaN, J. Crystal Growth 22, 44 (1974).
- III. E. Ejder, Refractive Index of GaN, phys. stat. sol. (a) 6, 445 (1971).
- IV. E. Ejder and P.-O. Fagerström, Photoconductivity of Zn-doped GaN, J. Phys. Chem. Solids (to be published).
- V. E. Ejder and H.G. Grimmeiss, Optical Investigations of Zn-, Hg-, and Li-doped GaN, Appl. Phys. (to be published).

The investigations have been carried out at the Department of Solid State Physics, Lund Institute of Technology, University of Lund, Box 725, S 220 07 Lund, Sweden.

Opto-electronics comprises both the basic physical phenomena and the behaviour of devices based on the interaction of electromagnetic radiation with the electrons in a solid. In general, these phenomena result either from the absorption of radiation, with consequent electronic effects, or from the generation of radiation by electronic transitions within a semiconductor.

This field has developed very rapidly during the last ten years, both in its fundamental and its applied aspects. The dual approach afforded by optical and electrical investigations has given valuable insight into the fundamental properties of semiconductors. In commercial research and device development, radiation detectors for a very wide spectral region have been successively developed over the years, while the fields of light-emitting diodes and semiconductor lasers are at present the subject of intense work.

The minimum wavelength, or the colour, of the light emitted by an electroluminescent material is determined by its band-gap. As the lower energy limit of the visible spectrum corresponds to an energy of about 1.7 eV, it is necessary to employ materials with band-gaps larger than this figure. The demand for light-emitting diodes has given a great impetus to the exploration of new semiconducting materials. The band-gaps of the two classic semiconductors Ge and Si are too small for such applications and hence interest has been directed towards binary, ternary and even more complicated compounds. One group of semiconductors which has attracted considerable interest is the III-V compounds, i.e. compounds consisting of one element from the third group of the periodic system, usually B, Al, Ga, or In, and one from the fifth, usually N, P, As, or Sb.

Of all the possible compounds formed by combinations of these elements, GaN has the attractive feature of a band-gap of 3.4 eV ($\sim 3600 \text{ \AA}$), just at the short wavelength limit of the visible

spectrum. This would in principle open up the possibility of getting recombination radiation in any arbitrary part of the visible spectrum by the introduction of properly-localized impurity levels by doping. The spectral sensitivity of the human eye peaks at about 2.2 eV (5600 Å), in the green part of the spectrum. The first generation of light-emitting diodes used for indicator lamps and in arrays for numeric or alphanumeric displays, which give red light, is thus by no means ideal.

From the standpoint of pure physics, GaN is of considerable interest being a wide, direct band-gap material with a high ionicity and showing anisotropy due to its hexagonal structure. From the standpoint of semiconductor devices, it is a material with potential applications as an electroluminescent material emitting light in any part of the visible spectrum.

The investigations of this thesis are contributions to our knowledge of the basic physical properties of GaN.

Epitaxy, the formation of a single crystalline layer which is oriented crystallographically with respect to the substrate, has been widely used for the preparation of single crystal material. This growth procedure is well adapted to many of the requirements of semiconductor device technology, making possible the deposition of layers well defined both in thickness and doping concentration. In addition, for the investigation of the fundamental physical properties of semiconducting materials, the epitaxial method of sample preparation has some advantages. In the case of GaN, for which crystal growth based on heterogeneous nucleation at normal pressures has yielded only small crystals in reasonable times, epitaxial layers have been the most common samples for investigations of GaN properties.

The original meaning of "epitaxy" was the growth of one substance on another. Most work with semiconductors, has, however, been concerned with the growth of a layer on a substrate of the same

material, e.g. Si on Si or GaAs on GaAs, for which the term "epitaxy" has been retained. As a consequence, a new term "heteroepitaxy" has been introduced for the situation in which the layer and the substrate consist of different materials. Till now, all epitaxial GaN has been prepared by heteroepitaxy due to the non-availability of reasonably large GaN crystals to serve as substrates. Recently, however, some improvements in the latter respect have been made (1).

Several different substrate materials have been tried: $\alpha\text{-Al}_2\text{O}_3$, SiC, Si, GaAs, GaP, spinel (2-7). It is well-known that the surface perfection of the substrate is of critical importance for the quality of the epitaxial layer and structural analysis of epitaxial layers of both elemental and compound semiconductors has shown a wide variety of lattice imperfections. Another important factor influencing the properties of the layer is the residual stress resulting from the differing thermal contraction cooling from the growth temperature. This difference obviously prevents the use of some substrate materials. In the case of GaN on (0001)-oriented $\alpha\text{-Al}_2\text{O}_3$, we always observe cracks, either in the GaN layers (for layer thicknesses $< 50 \mu$) or in the 250μ thick substrates (for layer thicknesses $> 50 \mu$). The development of actual cracks is evidence of very severe stress developing during the cooling to room temperature and must be expected to have a considerable influence on the optical and electrical properties of the samples. Taking the broadening of exciton lines in photoluminescence as a measure of the stress, we find that the layers must be at least of the order of 100μ thick to yield good spectra, which shows that the stress effects gradually decrease at the surface with increasing thickness.

The investigation presented in paper (I) was made to provide a future basis for judging the suitability of different substrate materials for epitaxial growth, from the thermal expansion aspect. Furthermore, it gives a necessary condition for the quantitative treatment of the stresses caused in GaN when grown in heteroepitaxy.

The considerable difficulties encountered in the synthetization of high quality GaN single crystals has been a limiting factor in the exploration of the properties of this material. Early investigations were made on powder samples and gave important results (8-10). However, powder samples have severe limitations. For example, the anisotropy of different properties is not distinguished, nor are significant electrical measurements possible. Preliminary investigations of small single crystals were also made at a rather early date (9). Since the successful growth of GaN by epitaxy was reported in 1969 (2), this method has been gradually improved. In spite of this, it is no ideal method for the preparation of crystals with a low density of lattice imperfections. Also, for the epitaxial method, it is important to have a knowledge of the morphology of unstrained crystals. In paper (II), the growth and morphology of GaN grown by heterogeneous nucleation by direct synthesis of gallium metal vapour and ammonia is studied. This method gives rather small crystals, but with a high degree of crystalline perfection and it might be a solution of the problem of getting GaN substrates for further epitaxial growth. The fact that the charge carrier concentration of these single crystals is obviously higher than that of the best epitaxial layers is not very important in this application.

The crystal structure is also studied in paper (II). Some related compounds, belonging to the II-VI or III-V families, crystallize in the hexagonal and some in the cubic structure with a limit at approximately $c/a = 1.633$. GaN with a ratio of 1.627 is very near this value and a cubic structure might be a possible alternative. This has, however, not been detected at normal temperatures and pressures. The growth mechanism is also discussed with respect to the crystal habits observed under various circumstances of growth.

Paper (III) reports measurements of the refractive index of as-grown GaN platelets having a charge carrier concentration of

about 10^{19} electrons cm^{-3} . Epitaxial layers have not the surface flatness and perfection required for a refractive index determination by the interference method which requires that variations in thickness are much smaller than the wavelength of the light in question. GaN has a hexagonal structure and has thus a non-isotropic refractive index. The platelets have their c-axis perpendicular to the plane of the crystal, but, by varying the angle of incidence, it has also been possible to determine the refractive index perpendicular to the c-axis. The temperature dependence of the refractive index was measured and compared with the theory of Yu and Cardona (11) giving an estimated value of 600 K for the Debye temperature of GaN.

The extrapolated value of ϵ_{∞} can be used to calculate the Phillips ionicity (12), giving a value of 0.5, which confirms that GaN is a high ionicity compound compared with other III-V compounds.

The temperature dependence of the band-gap energy of GaN is also reported in (III), as inferred from diffuse reflexion spectra of powder samples. It is pointed out that the relative change rather than the absolute value of the absorption threshold should be trusted, due to the method employed, and this judgement has been confirmed. The band-gap is now stated to be 3.503 eV at 0 K (13), while the agreement of the relative change in band-gap energy between paper (III) and (13) is very good.

The luminescent properties of GaN which are of interest for applications in the field of light-emitting devices are governed by the position and concentration of impurity centres in the material. This fact, together with the current general interest in the properties of deep levels in semiconductors, has been the background for the investigations presented in papers (IV) and (V).

GaN crystals which have not been intentionally doped and which are grown under circumstances intended to produce high purity

material always show n-type conductivity, the lowest charge carrier concentration reported being of the order of 10^{17} electrons cm^{-3} . For many applications, it would be desirable to be able to prepare p-type material also, thus making the manufacture of pn-junctions possible. Efforts to produce p-type GaN have so far been unsuccessful and the question as to whether it is possible is still open. However, it is possible to compensate the material closely, getting very high resistivities. The procedure of partial compensation has been used to prepare light-emitting nn^+ -junctions with interesting properties (14). The doping element which has attracted the greatest interest in this respect is Zn, since it gives strong, blue luminescence. However, the nature and properties of the luminescence centres caused by Zn have not been well understood.

Photoconductivity investigations are often useful for the study of impurity centres in semiconductors. Preliminary measurements in GaN were soon made (9), supporting the estimation of the band-gap energy. Having succeeded in preparing very high resistivity Zn-doped epitaxial GaN, the investigations presented in paper (IV), which reports features in extrinsic photoconductivity, have been made. It is shown that the Zn-doping actually causes centres which give free conduction band electrons when the sample is extrinsically excited. The excitation threshold energy corresponds closely to the short wavelength cut-off of the blue luminescence emission and has been studied as a function of temperature, suggesting that the level is pinned to the valence band.

In paper (V) the properties of the centres caused by Zn-doping are further clarified, together with properties of other dopants, Hg, Li, Cd, which cause luminescence centres in GaN. In this case, the method of infrared quenching of photoluminescence is used to study the spectral dependence of the photoionization cross-sections of these centres. This method is particularly valuable in the present case, for which investigations of pn-junctions are not possible. Together with other measurements reported in (V), these investigations contribute to our understanding of luminescence processes in GaN, in particular of Zn-doped material.

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